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## ABSTRACT

The performance of ablative thermal protection materials is generally evaluated in ground test facilities. Results of these tests are then used in analytical studies to predict the behavior of the materials during atmospheric reentry. The thermochemical properties of the ablation material, which are determined by studies of the decomposition of the material, must be used in these analyses.

The results of some recent studies of the pyrolysis of a charring ablator are presented in this paper. By employing thermoanalytical techniques, the thermochemical properties such as heat of pyrolysis, pyrolysis temperatures, and kinetic parameters describing mass loss have been determined. Analysis of the pyrolysis products have also been made. This information can now be used in analytical studies to predict more accurately the performance of this material on reentry vehicles. Although data will be presented for only one particular material, the methods described are applicable to the analysis of any heat-shield material of interest.

## INTRODUCTION

The use of ablation materials for heat protection on entry vehicles has been the subject of many experimental and analytical studies. Experimental studies, such as given in references 1 and 2, are generally employed to determine the relative performance of ablation materials in the simulated entry environment of ground test facilities. These studies have shown the specific effects of environmental parameters upon the performance of selected composite charring ablators. Analytical studies, for example, references 3 and 4, show the effects of various material parameters upon thermal performance properties. These studies have shown that a quantitative determination of the thermochemical properties such as heat of pyrolysis, pyrolysis temperatures, kinetic parameters which describe mass loss, and pyrolysis product composition are necessary in order that the performance of the charring ablator can be predicted more accurately. These quantities are determined by studies of the pyrolysis of the ablation material.

A limited quantity of thermochemical property data on polymeric materials is available (refs. 5, 6, and 7). However, the majority of these data are for polymers quite different from the multi-component ablation material and are invariably limited to the determination of a single facet of polymer decomposition. Consequently, analytical studies have been hampered by insufficient data on the thermochemical properties associated with pyrolysis. The specific purpose of this paper is to present the results of an investigation of a phenolic-nylon ablation material in which the thermochemical properties are determined. The desired thermochemical properties of the phenolic-nylon material are determined by differential thermal analysis (DTA), thermogravimetric analysis (TGA), pyrolysis gas chromatography, and elemental analysis.

## SYMBOLS AND UNITS

The units used for the physical quantities defined in this paper are given in the International System of Units (SI). Reference 8 presents factors relating this system to other frequently used systems.

A	frequency factor, $s^{-1}$
E	activation energy, J/mole
k	specific rate, $s^{-1}$
n	pseudo-order of reaction
R	gas constant, 8.314 joules/mole-°K
t	time, s
T	temperature, °C
$\dot{T}$	$dT/dt$ , temperature rise rate, °C/s
m	mass of material at temperature T, mg
$m_r$	mass of residue or char, mg
$m_0$	initial mass of material, mg

## ANALYSIS AND PROCEDURE

When a charring ablation material is exposed to the severe heat of the entry environment, the incident heat is initially absorbed and conducted into the material. When the surface temperature exceeds the pyrolysis temperature, a layer of carbonaceous residue (char) begins to form as a result of thermal decomposition. Figure 1 shows a cross section of an ablation material which has been exposed to a simulated entry environment. In this figure the char resulting from thermal decomposition of the ablation material, the pyrolysis zone and the unpyrolyzed plastic are shown. The decomposition of the ablation material results in the generation of a variety of volatile products of high and low molecular weight. These products move away from the decomposition zone through the char layer and into the boundary layer surrounding the ablation material. While passing through the hot char, the pyrolysis products experience thermal cracking to lower molecular weight species resulting in appreciable heat absorption. The injection of these pyrolysis products into the boundary layer lowers the enthalpy potential and thus reduces the convective heat to the surface. As the pyrolysis zone moves deeper into the ablation material and the char layer continues to increase in thickness, the surface

temperature increases considerably, resulting in an increase in radiation from the hot char surface. Thus the heat accommodation is the combined result of energy absorption as gases flow through the char layer, convective blocking, heat absorption by material pyrolysis, and heat capacity and insulation (see fig. 1).

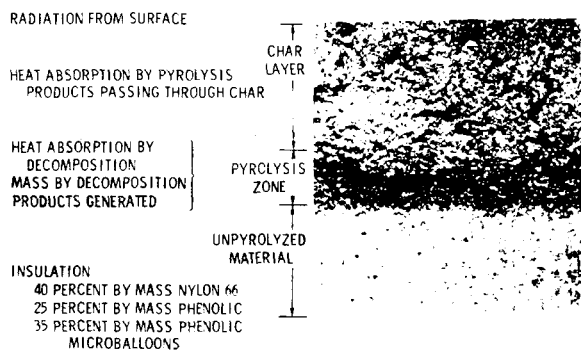


Figure 1.- Cross section of a charring ablation material.

### Material

The material investigated is a typical composite charring ablation material composed by mass, of 40% nylon 66, 25% phenolic binder, and 35% phenolic Microballoons (low-density filler). The characteristics of decomposition of this material are determined by studies of the decomposition of the individual compounds with several thermoanalytical techniques. The techniques, DTA, TGA, pyrolysis gas chromatography, and elemental analysis provide data on a particular phase of the decomposition processes. The characteristics of decomposition of the individual compounds are then used to aid in the interpretation of the decomposition of the ablation material.

### Pyrolysis

The techniques of DTA, TGA, and elemental analysis were employed to investigate the characteristics of the pyrolysis zone. Information on the mass loss of the ablation material was obtained using the technique of thermogravimetric analysis (TGA). In TGA, mass changes are recorded as a function of temperature as the temperature is increased at a constant rate. From the results, kinetic parameters are determined which describe the mass loss during decomposition. The mass loss of ablation materials (high molecular weight organic polymers) normally occurs through complex mechanisms which are not sufficiently understood to formulate exact analytical expressions from which the kinetic parameters describing mass loss could be determined. Empirical homogeneous kinetics normally suffice to describe the decomposition. By assuming the decomposition mass loss reactions to be irreversible, these reactions may be described by a form of the pseudo-order classical rate expression:

$$-\frac{1}{m_0} \frac{dm}{dt} = kf(m/m_0) \quad (1)$$

where the specific rate  $k$  is expressed by the Arrhenius relation;

$$k = Ae^{-E/R(T+273)} \quad (2)$$

The function  $f(m/m_0)$  usually has the form

$$f(m/m_0) = \left( \frac{m - m_r}{m_0} \right)^n \quad (3)$$

equations (1), (2), and (3) may be combined to form

$$-\frac{1}{m_0} \frac{dm}{dt} = \left( \frac{m - m_r}{m_0} \right)^n Ae^{-E/R(T+273)} \quad (4)$$

The kinetic parameters: activation energy  $E$ ; frequency factor  $A$ ; and order  $n$ ; are determined from this rate equation using the TGA mass loss data. The actual techniques used to evaluate these parameters are demonstrated in detail in references 9, 10, and 11. The pyrolysis temperatures (which indicate the width of the pyrolysis zone) and the energy absorbed or evolved during pyrolysis are determined by differential thermal analysis (DTA). In DTA, the total heat content of the sample material is continuously compared with that of an inert reference material while both are heated at constant temperature rise rate in the same environment.

### Pyrolysis Products

The products of pyrolysis are determined by pyrolysis gas chromatography. In order to determine these products, the sample is pyrolyzed in the entrance port of the gas chromatograph. In the gas chromatograph, the gaseous products are separated by means of a liquid-coated solid support which has been placed in a long column. The separating processes actually consist of a multiple partition between the liquid and gas phase. The identification of the fractionated products is based upon the time required for a given species to pass through the packed column. Also aiding in the analysis of the pyrolysis of the ablation material is the technique of elemental analysis. The elemental composition of the ablation material is determined at various pyrolysis temperatures and the elemental composition compared with the gaseous products identified by gas chromatography. Using this technique, the type of pyrolysis reaction can be deduced. The elemental composition is determined by burning the sample in 100% oxygen at 900° C. The products of this combustion, water and carbon dioxide for the carbon-hydrogen determination, are caught in previously weighted absorption tubes. The nitrogen determination was based upon pyrolysis in a carbon-dioxide atmosphere at 700° C. After passing over zones of copper oxide and reduced copper, the nitrogen is collected and measured over a potassium hydroxide solution in an azotometer.

### RESULTS

#### Pyrolysis

Differential thermal analysis.- The DTA thermograms of the three components which compose the phenolic-nylon composite ablation material are shown in figure 2. The results shown were obtained by heating the material at 10° C/min in a helium atmosphere to the temperature shown. The reactions which occurred upon heating are shown as either endothermal or exothermal with the endothermal

reactions extending downward from the base line  $\Delta T = 0$  and the exothermal reactions extending upward from the base line. At the top of figure 2 is shown the thermogram of nylon. The specimen was observed to pass through two endothermic processes, one with peak at  $260^{\circ}\text{C}$  and the second at approximately  $417^{\circ}\text{C}$ . The first endotherm is associated with the melting of the crystalline portion of the polymer (heat of fusion =  $73.6\text{ kJ/kg}$  of original material) while the second corresponds to decomposition. The decomposition, which occurs between  $350^{\circ}$  and  $500^{\circ}\text{C}$ , absorbs  $630\text{ kJ/kg}$  of original material. The apparent exothermal portion of the thermogram after  $470^{\circ}\text{C}$  results from the change in total heat capacity accompanying decomposition.

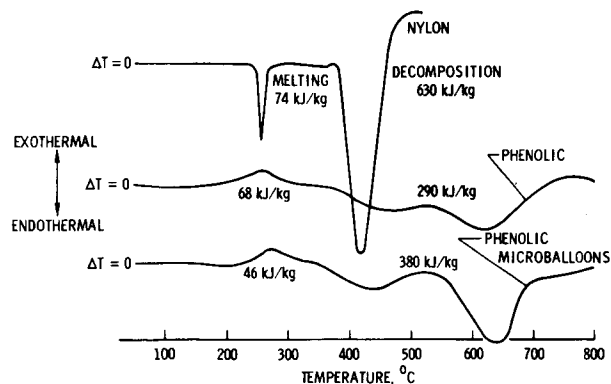


Figure 2.- Differential thermal analysis thermograms of nylon, phenolic, and phenolic Microballoons.

The center thermogram of figure 2 is for phenolic used as the binder in the composite phenolic-nylon material. This material is formed from a commercial novolac resin. The reactions observed upon heating this polymer were found over the temperature range between  $150^{\circ}$  and  $850^{\circ}\text{C}$ . The thermogram shows an exothermal reaction at  $265^{\circ}\text{C}$  followed by two overlapping endothermal decomposition reactions at  $450^{\circ}$  and  $625^{\circ}\text{C}$ . The exothermal reaction evolves  $68\text{ kJ/kg}$  and the pyrolysis reactions between  $350^{\circ}$  and  $850^{\circ}\text{C}$  absorbed  $293\text{ kJ/kg}$ . The thermogram in the lower portion of figure 2 corresponds to the decomposition of phenolic

Microballoons. This material consists of small hollow microspheres of phenolic, formed from a resole-type resin. The decomposition thermogram of this material is very similar to that of the binder phenolic shown in the center of figure 2. The exothermal reaction at  $270^{\circ}\text{C}$  evolves approximately  $47\text{ kJ/kg}$  while the two overlapping endothermal pyrolysis reactions between  $350^{\circ}\text{C}$  and  $850^{\circ}\text{C}$  absorb  $377\text{ kJ/kg}$ .

**Thermogravimetric analysis.**- Figure 3 shows the results of thermogravimetric analysis of the three separate constituents. The residual mass fraction is plotted as a function of temperature. The TGA data are obtained by heating the materials at  $9^{\circ}\text{C/min}$  in a reduced pressure of  $65\text{ N/m}^2$  ( $0.5\text{ torr}$ ). The TGA thermogram of nylon shows one sharp mass loss between  $350^{\circ}$  and  $500^{\circ}\text{C}$ . Almost all of the nylon mass is converted to gaseous products through this temperature range, with less than 10% remaining at  $500^{\circ}\text{C}$ . The TGA thermogram of phenolic and phenolic Microballoons, also shown in figure 3, shows the mass loss of these materials to continue through  $850^{\circ}\text{C}$ . The residue of both phenolic materials was determined to be approximately 54% of their original mass.

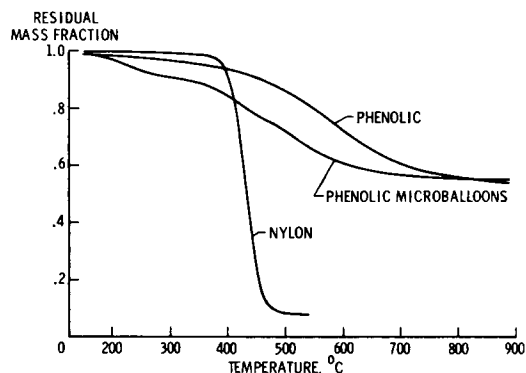


Figure 3.- Thermogravimetric analysis thermograms of nylon, phenolic, and phenolic Microballoons.

The results of analysis of the three materials used in the composite phenolic-nylon material are summarized in table I. The nylon decomposition

TABLE I.- KINETIC PARAMETERS OF NYLON, PHENOLIC, AND PHENOLIC MICROBALLOONS

Material	Reaction(s)	Reaction temperature (peak temperature),	Activation energy $E$ ,	Frequency factor $A$ ,	Reaction order $N$
		$^{\circ}\text{C}$	$\text{kJ/mole}$	$\text{sec}^{-1}$	
Nylon	1	417	232	$8.3 \times 10^{14}$	1.0
Phenolic	3	275	114	$5.1 \times 10^8$	3.0
		450	100	$2.5 \times 10^5$	1.3
		625	140	$2.0 \times 10^7$	3.1
Phenolic Microballoons	3	270	70	$2.0 \times 10^5$	2.0
		435	122	$9.7 \times 10^6$	2.0
		630	172	$1.3 \times 10^{10}$	3.0

reaction, with peak maximum at 417° C, was determined to have an activation energy of 232 kJ/mole and be of order one. The three reactions observed in each phenolic were found to yield activation energy values ranging from 70 kJ/mole to 172 kJ/mole and reaction order extending to 3.1. The data shown in table I will be used to compute the mass loss of the composite ablation material and a comparison of this computed mass loss and the experimental data will be made in the following section.

**Analysis of the composite material.**— Figure 4 shows the decomposition reactions and mass loss (DTA and TGA thermograms, respectively) for an ablation material consisting of 40% nylon, 25% phenolic, and 35% phenolic Microballoons, by mass. The reactions involved in the decomposition of the individual components, the melting peak and decomposition endotherm of the nylon component, are easily observed superimposed on the decomposition reactions of the two phenolic constituents.

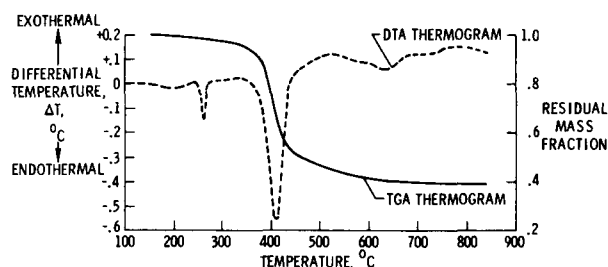


Figure 4.— DTA-TGA results of phenolic-nylon composite ablation material.

The TGA thermogram of the composite material shows the total mass loss of the phenolic-nylon ablation material to be 65%. This corresponds to the total mass loss expected from the mass loss of the individual constituents.

**Elemental analysis.**— The results of analysis of the elemental composition of phenolic (binder material) are shown in table II. The elemental composition of the material is determined at various temperatures and includes the composition of the residue through the decomposition range. By employing these data and the mass loss data from TGA, it is possible to calculate the residual mass

TABLE II.— RESULTS OF ELEMENTAL ANALYSIS

Temperature, °C	Percent by mass			
	Carbon	Hydrogen	Nitrogen	Oxygen
Ambient	75.60	6.12	2.35	15.93
150	76.08	5.81	2.02	16.09
200	76.98	5.82	1.72	15.48
300	77.14	5.60	.78	16.48
400	78.45	5.42	.42	15.71
450	79.40	5.36	.40	14.84
500	81.53	4.89		13.58
550	84.22	4.47		11.31
600	88.00	3.59		8.41
650	90.81	2.85		6.35
750	92.31	1.54		6.15
850	92.65	.90		6.45

fraction data for each element. The results of this calculation are shown in figure 5, where the elemental residual mass fraction is plotted as a function of pyrolysis temperature. The actual change in composition of the polymer as a function of pyrolysis temperature is shown in figure 6. The unpyrolyzed material, as shown in table II, contained 75.6% carbon, 6.12% hydrogen, 15.93% oxygen, and 2.35% nitrogen. The high percentage of nitrogen was found to be a result of trapped species from the curing agent, hexamethylenetetramine. The loss of species (fig. 5) containing this element, at low temperature and before decomposition occurred again shows this entrapment within the solid cross-linked polymer. The mass loss by decomposition, shown between 350° and 850° C in the TGA thermogram of figure 3, is again observed in the residual mass fraction (data shown in fig. 5).

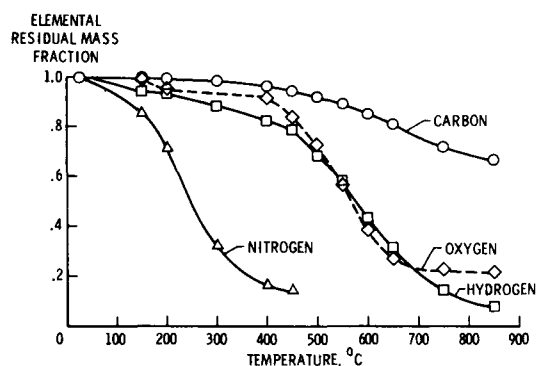


Figure 5.— Elemental residual mass fraction for decomposition of phenolic.

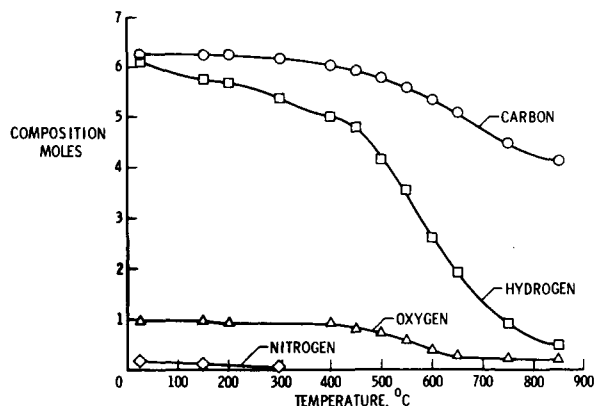


Figure 6.— Elemental composition for residue and char from decomposition of phenolic.

### Pyrolysis Products

From the TGA data of figure 3, it was observed that approximately 90% of the nylon and approximately 46% of the two phenolic materials were converted to gaseous products. The quantitative identification of the various species evolved by decomposition of phenolic was made by pyrolysis gas chromatography. Table III shows the results of analysis of the decomposition products of phenolic (binder material). The various species identified are shown at the top of each column and the quantity of each component found is shown at the base

TABLE III.- PRODUCT DISTRIBUTION FROM DECOMPOSITION OF PHENOLIC

Temperature, °C	Percent of total moles identified								
	CO <sub>2</sub>	CO	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>6</sub> H <sub>5</sub> ·OH	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ·OH	CH <sub>4</sub>	H <sub>2</sub> O	H <sub>2</sub>
100								1.47	
150								.75	
200								.48	
250								.57	
300								1.28	
350								3.44	
400					0.46	0.13	0.05	3.44	
450		0.21			.81	.25	.15	5.42	0.76
500	0.09	.44	0.02	0.08	2.72	.75	.75	3.35	1.47
550	.11	.87	.06	.13	1.62	.38	1.29	2.44	2.18
600	.32	1.30	.06	.05	.79	.14	2.61	.40	3.65
650	.51	1.19	.03	.04	.44	.10	2.35	.26	5.17
700	.26	.77		.01	.21	.05	1.32	.13	5.88
750	.17	.54			.09		.83		6.64
800	.11	.26					.40		7.35
850		.20					.20		5.88
900							.08		4.50
950									3.65
1000									2.94
Total	1.6	5.5	0.2	0.3	7.1	1.8	10.0	23.4	50.1

of each column. As shown in this table, the largest component found was hydrogen (50.1%) while water and methane were found as 23.4% and 10.0% of total moles, respectively. The product evolution curves corresponding to the identified species are shown in figures 7 and 8 where the percent of total moles identified is plotted as a function of decomposition temperature. In figure 7 are shown the evolution curves of water, hydrogen, and methane from pyrolysis of phenolic. Similar curves for phenol, xyleneol, and carbon monoxide are shown in figure 8. The distribution curves of the remaining products of phenolic pyrolysis were not plotted. It should be noted that these data (table III) are based upon only those products which were identified and do not reflect any lost species such as species with high boiling points which condense in the entrance part of the gas chromatograph and thus are not detected.

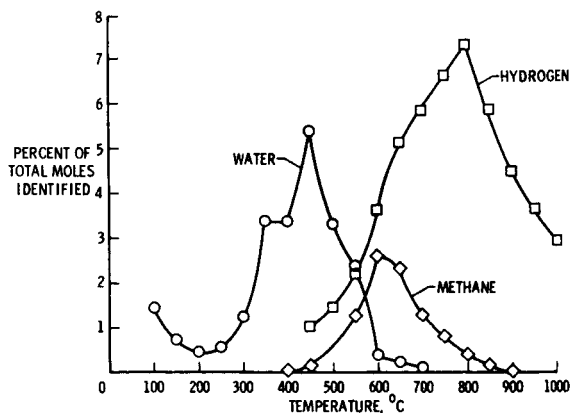


Figure 7.- Pyrolysis product analysis for phenolic.

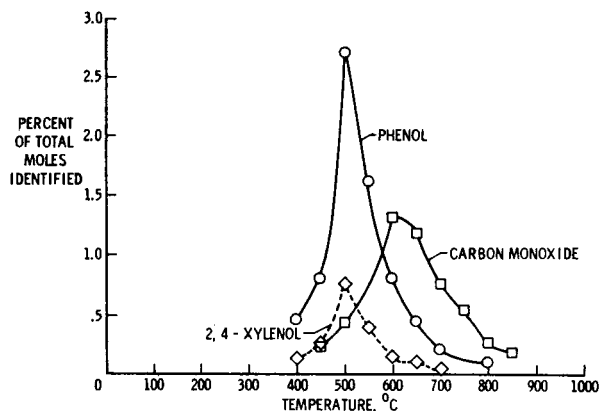


Figure 8.- Pyrolysis product analysis of phenolic.

#### DISCUSSION OF RESULTS

Transpiration of gases through the char layer is a major part of the heat accommodation characteristics of a charring ablator, as indicated in reference 3. In order to determine the effects of this mechanism upon the performance of a charring ablator, it is desirable to determine the products generated by pyrolysis. Complete data covering the analysis of the products generated by pyrolysis of the phenolic-nylon ablator are not available; however, the products of one of the constituents of the ablation material have been determined. Pyrolysis product analysis of the phenolic (binder material) of the composite material indicates that the major component of decomposition is hydrogen (50% of total moles observed). Water, methane, and phenol are observed as 23.4%, 10%, and 7.1% of total moles, respectively. These results appear to be in good agreement with those given in reference 5, where the

decomposition product analysis of a phenolic (formed from resole resin) is given. The distribution of many of the identified pyrolysis products over the temperature range investigated is given in figures 7 and 8. By comparison of these distribution curves with the DTA and TGA thermograms of figures 2 and 3, it is possible to associate specific products with observed reactions. Water, for example, is observed to evolve at low temperatures and through the temperature range of thermal decomposition, as shown in figure 7. At low temperatures this water evolution is associated with the exothermal reaction observed on the DTA thermogram of figure 2. The exothermic nature of the thermogram and the low temperatures involved imply a curing reaction from which water is the principal product. It is, therefore, postulated that a curing reaction which results in the cleavage of -OH groups is the source of this water. It is also noted from figures 1 and 7, that the maximum point in the evolution curve of water also approximately marks the onset of production of many other species which are attributed to thermal breakdown of the material. Further comparison of the TGA-DTA thermograms with the pyrolysis gas evolution curves shows that several specific products can be associated with each of the decomposition reactions of the material. The endothermic reaction between 375° and 500° C, with peak at approximately 450° C, is easily correlated with a fragmentation mechanism which results in depolymerization-type products such as phenol and xylenol. The second of the endothermic reactions located between approximately 500° and 800° C and with peak at 625° C is associated with a fragmentation mechanism which results in oxidative-type products such as carbon monoxide and carbon dioxide and other products such as methane and hydrogen. This type of product implies that a more complete breakdown of the polymer structure is occurring. These results show that char formation is a consequence of the endothermic decomposition reaction centered at approximately 625° C (DTA peak). The results of elemental analysis, figure 5, also show the residue to have its greatest increase in carbon content through this temperature range (500° to 800° C) and correspondingly its greatest loss of species containing oxygen and hydrogen.

The overall decomposition of the composite ablation material shown by DTA-TGA results in figure 4 covers a wide temperature range (200° C to 850° C). This decomposition width is observed to be a result of phenolic decomposition. Through this range, the heat absorption by decomposition was found to be 469 kJ/kg of original material; however, the greatest area of heat absorption is that between 350° C and 475° C, where nylon decomposition occurs. The mass loss of the composite material is also greatest through this narrow temperature range. The pyrolysis zone of an ablation material is defined in ablation material performance studies as that area of decomposition where the rate of mass loss, heat absorption, and gas evolution are at a maximum and the material passes from an unpyrolyzed polymer composite to a carbonaceous char. The DTA-TGA thermograms of figure 4 show this area to correspond to the temperature range between 350° and 475° C. The decomposition of phenolic thus has little, if any, effect upon the choice of this reaction zone position since the large mass loss and heat absorption are a direct result of nylon decomposition. Since it is often assumed that pyrolysis (decomposition of the

ablation material to a char) occurs in a plane or very narrow zone, it is advantageous to compare the center of this reaction zone (from DTA) or maximum rate of pyrolysis (from TGA) with the actual temperature of char production. This comparison shows that there is a 200° C temperature difference between the center of these important mechanisms; or, in terms of actual distance, reference 4 indicates that this temperature difference could correspond to as much as 3 millimeters in the ablation material.

The kinetic parameters which describe the mass loss of decomposition can also be used to describe certain physical characteristics of the reaction zone of the ablation material as pointed out in reference 4. In this reference, it was shown that the reaction zone thickness for a frequency factor (A) of  $10^{12} \text{ s}^{-1}$  is approximately one-half that for a frequency factor of  $10^8 \text{ s}^{-1}$ . The results of TGA data of the constituents of the phenolic-nylon ablator have shown that the frequency factor (A) for the endothermic decomposition of nylon is the order of  $10^{15} \text{ s}^{-1}$  while the frequency factors associated with phenolic decomposition were found to be as low as  $10^5 \text{ s}^{-1}$ . Thus, the high-frequency factor observed for the nylon decomposition reaction tends to result in a decrease of the reaction zone width, while the decomposition reactions of phenolic (binder and low-density filler) tend to result in an increase in this zone width.

Using the parameters which describe mass loss (determined from TGA and given in table I) for the individual constituents and assuming that in the composite phenolic nylon no interaction between components occurs, it is possible to calculate a mass loss curve for the composite material. This is obtained by integrating the rate equation shown previously (eq. (4)) and solving for mass in terms of the kinetic parameters and temperature. One equation is obtained for each reaction and each is weighted according to the relative percentage of the component in the total. The weighted equations are then added algebraically to yield an equation which describes the mass loss of the composite material. The result of this computed mass loss is compared with the experimental results in figure 9. It is observed that the computed mass loss curve is displaced to a higher temperature through the region of maximum decomposition (350° C to 500° C). However, the shape of the two curves and the mass loss involved in each reaction zone compare favorably. These results, as well as the DTA-TGA results of figure 4, indicate that the basic pyrolysis of this material is composed of an overlapping of the decomposition reactions of the individual polymers which compose the ablator.

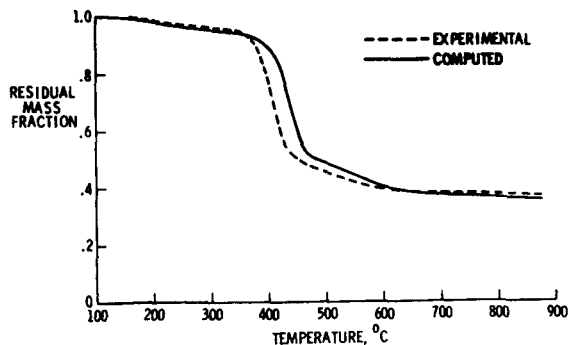


Figure 9.- Comparison of computed and experimental TGA thermograms.

## CONCLUDING REMARKS

The results of thermoanalysis studies of a phenolic-nylon charring ablation material and the individual constituents which comprise this ablator, have provided a detailed examination of the individual pyrolysis mechanisms from which much of the reentry thermal protection provided by this material is derived. From these studies, the thermochemical properties necessary for theoretical analysis of the performance of the material have been determined. Specifically, the heat of pyrolysis, pyrolysis temperatures, and kinetic parameters which describe mass loss for nylon, phenolic, phenolic Microballoons, and the phenolic-nylon ablator were determined. The quantitative identification of the pyrolysis products of one component (phenolic) of the ablation material was given and these results employed, with the aid of residue and char analysis, to identify the type of reaction occurring through decomposition.

In addition to these general results, the following conclusions concerning the effects of decomposition characteristics upon the charring ablator were reached:

1. The pyrolysis zone of the phenolic-nylon ablator is located between  $350^{\circ}\text{C}$  and  $475^{\circ}\text{C}$  and in the range of nylon decomposition.
2. Eighty percent of the observed total mass loss occurs through the pyrolysis zone defined by the temperature range between  $350^{\circ}\text{C}$  and  $475^{\circ}\text{C}$ .
3. The pyrolysis zone position is independent of the effects of phenolic decomposition.
4. The char production of the ablation material occurs in a reaction at approximately  $625^{\circ}\text{C}$  or nearly  $200^{\circ}\text{C}$  after the center of the pyrolysis zone.

## REFERENCES

1. Dow, M. B.; Swann, R. T.: Determination of Effects of Oxidation on Performance of Charring Ablators. NASA TR R-196, 1964.
2. Clark, R. K.: Effect of Environmental Parameters on the Performance of Low-Density Silicone-Resin and Phenolic-Nylon Ablation Materials. NASA TN D-2543, 1965.
3. Swann, R. T.; Dow, M. B.; and Tompkins, S. S.: Analysis of the Effects of Environmental Conditions on the Performance of Charring Ablators. Journal of Spacecraft and Rockets, Vol. 3, No. 1, January 1966.
4. Stroud, C. W.: Study of the Chemical Reaction Zone in Charring Ablators During Thermal Decomposition. Presentation to the American Institute of Chemical Engineers, Dallas, Texas, February 6-9, 1966.
5. Shulman, G. P.; and Lochte, H. W.: Thermal Degradation of Polymers. II. Mass Spectrometric Thermal Analysis of Phenol-Formaldehyde Polycondensates. Journal of Applied Polymer Science, Vol. 10, 1966.
6. Friedman, H. L.: Kinetics of Thermal Degradation of Charring Plastics. Report No. R61SD145 Space Science Lab., General Electric Company, Aug. 1961.
7. Madorski, S. L.: Thermal Degradation of Organic Polymers. Interscience Publishers. New York, New York.
8. Mechtly, E. A.: The International System of Units - Physical Constants and Conversion Factors. NASA SP-7012, 1964.
9. Farmer, R. W.: Thermogravimetry of Plastics. Part I - Empirical Homogeneous Kinetics. ASD-TDR-62-1043; Part I, Feb. 1963. DDC Doc. No. AD40402999.
10. Doyle, L. D.: Evaluation of Experimental Polymers. (WADD Tr 60-283, ASTIA No. AD 243-387L) General Electric Company, June 1960.
11. Anderson, D. A.; and Farmer, E. S.: The Kinetics of the Thermal Degradation of Polystyrene and Polyethylene. J. of Polymer Science, Vol. 54, No. 159, Sept. 1961.